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ON MARIS AND HULBURT'S ULTRAVIOLET LIGHT THEORY OF AURORÆ AND MAGNETIC STORMS

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In a series of papers, Maris and Hulburt have developed an ultraviolet light theory of auroræ and magnetic storms.[1] The theory is not subject to the difficulty pointed out by Schuster and by Lindemann against the corpuscular theory, and is claimed to give a satisfactory explanation of the concentration of the auroræ in the region of high latitudes, the diurnal variations of magnetic storms, etc. The theory is based on the following assumptions: (1) The $\sim 10^{16}$ atoms or molecules (called simply particles here) in a column of unit cross-section above $\sim$ 450 km. bounce up and down with exceedingly long free paths and make $\sim 10^{14}$ collisions per second at the 450 km. level. The particles at this level are excited to high energy states or ionized by solar radiations. In collisions of the second kind with these excited particles or in collisions with recombining particles, the particles from above receive energies corresponding to velocities as high as 10 km./sec. It is assumed that some 10^{8} of these 10^{14} collisions are of this nature. The particles will reach some 40,000–80,000 km. in 3 to 6 hours. (2) These high flying particles are ionized by solar radiations in 3 to 6 hours and, being now electrically charged, come down in spirals around the lines of force of the earth's magnetic field. These ions coming down into the lower atmosphere produce the auroræ, etc.

This theory has been examined by Chapman and its consequences have been compared with the observed facts.[2] Mitra and Banerjee have made some calculations on the basis of this theory and obtained somewhat different values for the number of particles sent up per second and the time

[1] H. B. Maris and E. O. Hulburt, *Phys. Rev.*, 1929, **33**, 412; Hulburt, *ibid.*, 1929, **34**, 344; 1930, **36**, 1560; *Rev. Mod. Phys.*, 1937, **9**, 44.

[2] S. Chapman, *Monthly Notices, Roy. Astro. Soc. Geophys. Supp.*, 1930, **2**, 296; *Terr. Mag.*, 1938, **43**, 77. These papers are not available to the writer who comes across reference to the first in the articles by Hewson, *Rev. Mod. Phys.*, 1937, **9**, 430, and Hulburt, *Phys. Rev.*, 1930, **36**, 1560, to the second in *Science Abstracts*, No. 2814, 1938.

taken for the ionization of these particles.[3] The purpose of this note is to examine more closely the fundamental processes assumed by Maris and Hulburt and the calculations of Mitra and Banerjee.

Granting that the distribution of particle density with height is what the original authors assume, we can show that the number of particles receiving a high velocity by the assumed mechanism is extremely small. Consider first the possibility of a particle acquiring a high velocity by a collision of the second kind with an excited atom or molecule at the 450 km. level. The ratio of the concentrations of particles in an excited state k and in the ground state i may be expected to differ greatly from the Boltzmann factor on account of the low pressure and hence the scarcity of collisions in the upper atmosphere. To obtain the relative populations it would be necessary to treat the problem as one of radiative equilibrium in diluted temperature radiation according to the theory of cycles of Rosseland. For the consideration of the order of magnitude only, we may simplify the problem by considering only the state i, the state k and the continuum c so that we have

$$N_i B_{i\uparrow}^{k} \rho(\nu) + N' \int_0^\infty v\, Q(v)\, N_e(v)\, dv = N_k A_{i\downarrow}^{k} + N_k \int_{\nu_0}^\infty \frac{\tau(\nu)}{h\nu} I(\nu)\, d\nu, \qquad (1)$$

where N_i, N_k, N', $N_e(v)\,dv$ are the concentrations of particles in the states i, k and the ionized state, and of electrons having velocities between v and $v + dv$, respectively, $Q(v)$ is the cross-section for electron capture by the ion into the state k, $\tau(\nu)$ the cross-section for photo-ionization of the state k, $I(\nu)$ the intensity of solar radiation of frequency ν, and $B_{i\uparrow}^{k}$ and $A_{i\downarrow}^{k}$ are the Einstein coefficients of absorption and spontaneous emission respectively. It can readily be verified that the second term of the right-hand side of (1) is very small compared with the first, and for electron capture cross-section of the order 10^{-21} cm.[2] and total electron density less than 10^6/c.c., the second term on the left of (1) is small compared with the first so that approximately

$$N_k/N_i = (g_k/g_i)\, B_{i\downarrow}^{k} \Big/ A_{i\downarrow}^{k} = \frac{g_k}{g_i} \frac{c^3}{8\pi h\nu^3} \rho(\nu), \qquad (2)$$

where $\rho(\nu)$ is the radiation energy density at frequency ν, $h\nu = E_k - E_i$ and the g's are the statistical weights. ρ can be taken to be W times that of a black body at $T = 6000°$ K. where W is the dilution factor and is $\sim 5 \times 10^{-6}$. For $E_k - E_i = 13$ volts so that one half of it when transferred to a colliding particle of the mass of an oxygen atom may give it a velocity ~ 9 km./sec.,

[3] S. K. Mitra and A. K. Banerjee, *Indian J. Phys.*, 1939, **13**, 107.

the above ratio N_k/N_i is $\sim 10^{-16}\, g_k/g_i$. Thus of the 10^{14} collisions between the particles from above and those below, only $\sim 1/10^2$ of a collision takes place with an excited atom or molecule. Furthermore, the probability of energy transfer from an excited atom or molecule to a heavy particle is known to be very small, probably of the order of $10^{-3} - 10^{-1}$ per collision, when the energy must go into the kinetic energy of translation of the heavy particle. This small probability is due to the great disparity in the masses of the electron and the heavy particle. Hence of the 10^{14} collisions, only $10^{-5} - 10^{-3}$ of a collision, not 10^8 as Maris and Hulburt assumed, will result in imparting a high velocity to the particle from above.

Consider next the plausibility of a particle from above acquiring a high velocity on collision with recombining particles below. Now this is a three-body process and as such the probability is extremely small on account of the low pressure in the upper atmosphere. This probability can be expressed in terms of a cross-section of the recombination for unit concentration of the third body. On making an optimum assumption that the probability of the energy transfer in a given collision is $\sim 1/100$, this cross-section for unit concentration of the third body is $\sim 10^{-42}$ cm^5.[4] At a height where the concentrations of the recombining particles and of the third body are all of the order 10^{10}/c.c., the number of 3-body collisions is about 10^{-7} per second per c.c. Thus the number of particles acquiring a high velocity from recombining particles is too small to play any role in producing auroræ.

Consider now the calculations of Mitra and Banerjee for the number of particles sent up in collisions of the second kind between an atom and an oxygen atom in the metastable state ^1S formed by the capture of an electron by an oxygen ion O^+ produced by photo-ionization. The probability of ionization is given, as in (1), by

$$w = \int_{\nu_0}^{\infty} \frac{\tau(\nu)}{h\nu} I(\nu)\, d\nu \qquad (3)$$

where the atomic absorption coefficient $\tau(\nu)$ is $\sim 1{\cdot}4 \times 10^{-17}$ according to Bates, Buckingham, Massey and Unwin.[5] One has then $w \sim 1 \times 10^{-8}$ so that of the 10^{16} particles in a column of unit cross-section above ~ 770 km., about 1×10^{-8} are ionized per second. The number of recombinations forming O (^1S) in the column per second is given by $q = \alpha\, N_+\, N_-\, L$ where α is the recombination coefficient for radiative process, N_+, N_- are the

[4] *Cf.* H. S. W. Massey, *Negative Ions*, Cambridge Univ. Press, 1938.

[5] Bates, Buckingham, Massey and Unwin, *Proc. Roy. Soc.*, 1939, A 170, 322.

concentrations of O^+ and electrons and L is the height of the column such that $N_+ L$ = total number of O^+ in the column. Now Mitra and Banerjee obtained a value 10^5 for q by putting $q = \alpha\ n_+\ n_-$ where n_+, n_- are the numbers of O^+ and electrons produced in the column per second, a procedure which is obviously incorrect. To obtain an estimate of q, we need, not the numbers of O^+ and electrons produced per second in the column, but the concentrations and the total numbers present at a certain moment. The total number of O^+ in the column after irradiation by solar radiations for some 10^4 seconds (a few hours) is of the order 10^{12}. This number of O^+ and hence also of electrons must be spread over a great height so that the electron density N_- is probably of the order 10^3/c.c. (it cannot be much greater, for otherwise it would have been revealed by observations on the reflection of radio waves). As α is of the order 10^{-13} according to Bates *et al.*,[5] one finds for q a value $\sim 10^2$ per second. As the lifetime of the state ^1S of OI is 0·5 second and as the collision frequency at the level 800–900 km. is about one in 75 seconds, these 10^2 O (^1S) atoms make about 1 collision per second with other atoms. Of this only a fraction, say γ, will be of the second kind, where γ is the efficiency of energy transfer and is certainly less than unity. It is then clear that the process considered by Mitra and Banerjee is inadequate in accounting for the auroræ and magnetic storms. Incidentally it may be pointed out that the 4·2 volts of energy released in the process $^1S \rightarrow {}^3P$ in the oxygen atom will be divided between the two colliding atoms on momentum considerations so that the energy available for shooting the atom is only about 2 volts.

The above considerations also make it clear that no material changes in order of magnitudes of the various quantities will be obtained for the case of an active sun.

Finally, the assumption that the high flying atoms are ionized by solar radiations in 3 to 6 hours is based on the relation

$$E = t\,(I_0 - I) = t\,I_0\,(1 - e^{-\tau}), \tag{4}$$

where E is the ionization potential of the particle, t is the time in which the particle is ionized, I_0 and I are the intensities of the ionizing radiations before and after traversing a column of unit cross-section and of such height that it contains just one particle, and τ is the atomic absorption coefficient defined by the usual relation $I = I_0\ e^{-N\tau x}$. Mitra and Banerjee employed the relation (4) and found $t = 3 \times 10^3$ hours. Now the above relation for t implies that the atom continues to absorb energy from the radiation beam for a time t until it amounts to the ionization potential E. This is entirely at variance with the basic idea in the quantum theory in which the

process is governed entirely by probability considerations. The time t should be given by the relation

$$t = 1/w, \tag{5}$$

where w is the number of transitions per second from the bound state to the continuous state under the action of the radiation field. As ionization can be effected by all radiations with frequency ν greater than the value ν_0 corresponding to E, the total probability of ionization by solar radiations is simply that given by (3) and is of the order 10^{-8} per second. Hence the lifetime of the neutral oxygen atom is $\sim 10^8$ seconds instead of the values assumed by Maris and Hulburt and calculated by Mitra and Banerjee on the basis of (4).

Thus on the above general considerations, it is clear that the assumed physical picture of the processes invoked in the theory of Maris and Hulburt is inadequate for explaining the cause of auroræ and magnetic storms.

ELECTROLYTIC SOLUTION PRESSURE OF COPPER WIRES UNDER STRAIN

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Received January 25, 1943
(Communicated by Prof. N. K. Sethi, D.Sc., F.A.Sc.)

It is long since known that the tension existing on the surface of the metals has a considerable influence on the potentials of the metals in solution of its salts and therefore it has been found necessary to fix definite conditions for the preparation of the electrodes.

Uptil now no systematic study has been undertaken to establish a relationship between these strains and the electrolytic solution pressures. This is clearly due to the fact that strains are difficult to measure. The solitary instance of an attempt to study the effect is by M. G. Moore[1] who had done experiments to determine any change in the energy of emergence with change in the state of strain of the metal surface. The difference between the energy of emergence of the strained and unstrained surfaces was measured by the difference in the contact potential. His experiments showed that with an expansion of 1% the change in the energy of emergence was certainly less than 4×10^{-3} volts. His experiments were not intended to investigate any relation between strain and electrolytic solution pressure and therefore are of little use.

The experiments mentioned herein are an attempt for a systematic study of P. D. between strained and unstrained metallic surfaces dipping in solution of a metallic salt. As a result it is found that molecular aggregation on the surface of the strained wires plays an important part in the values of potential differences.

For the purpose of these experiments two copper wires were annealed by heating them till red hot and then dipping in methyl alcohol. This treatment has been found to give reversible copper electrodes. An electrolytic cell was prepared as shown in Fig. 1, one of the wires marked A was loose and without any strain while the other wire B was strained by suspending weights.

The cell C was filled with copper sulphate solutions of definite and known strength. An E.M.F. was found to develop between the strained and unstrained wires. The galvanometer used was a suspended coil mirror type made by Cambridge Instrument Co., Ltd., England, and had a sensitiveness giving 1 m.m. deflection for a current of 4×10^{-9} amp. The

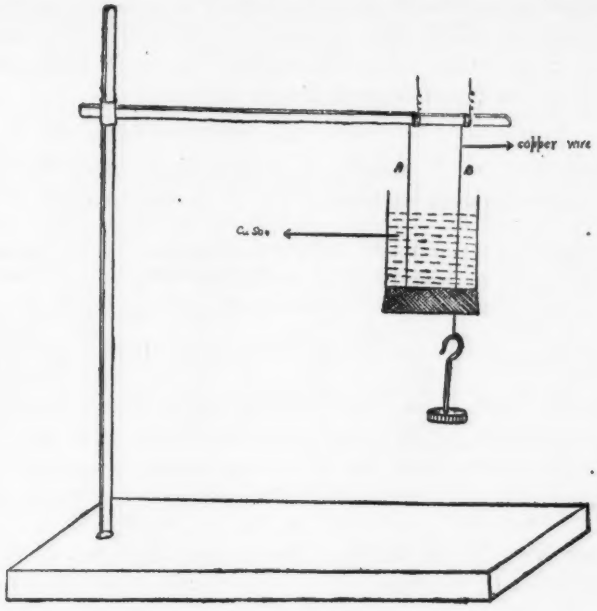
copper wire
A
B
Cu SO4

FIG. 1

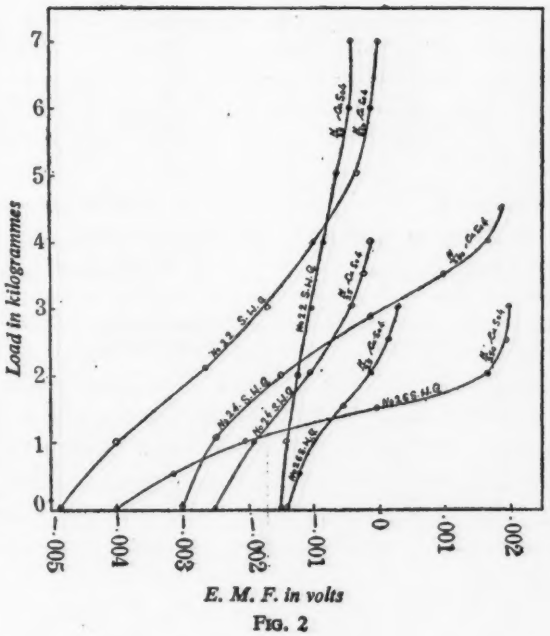
Load in kilograms
7
6
5
4
3
2
1
0
005
004
003
002
001
0
100
200
E. M. F. in volts

FIG. 2

resistance of the galvanometer was 450 ohms. The arrangement permitted the fall of potential of ·00001 volt being easily detected. The measurements were made by a potentiometric arrangement. The results of the experiments have been shown in the tables and graphs attached.

TABLE I

The Copper Wire No. 22 S.W.G. in N/25 Copper Sulphate Solution

Load applied (Kilogrammes)	E.M.F. Observed
0	−·0015 volt
1	−·0014
2	−·0012
3	−·0010
4	−·0008
5	−·0006
6	−·0004
7	−·0004

TABLE II

The Copper Wire No. 24 S.W.G. in N/25 $CuSO_4$ Solution

Load applied (Kilogrammes)	E.M.F. Observed
0	−·0025 volt
1	−·0019
2	−·0010
3	−·0004
3·5	−·0002
4	−·0001

TABLE III

The Copper Wire No. 26 S.W.G. in N/25 $CuSO_4$ Solution

Load applied (Kilogrammes)	E.M.F. Observed
0	−·0014 volt
0·5	−·0012
1	−·0010
1·5	−·0005
2	−·0001
2·5	+·0002
3	+·0003

TABLE IV

The Copper Wire No. 22 S.W.G. in N/250 $CuSO_4$ Solution

Load applied (Kilogrammes)	E.M.F. Observed
0	−·0049 volt
1	−·0040
2	−·0025
3	−·0017
4	−·0010
5	−·0003
6	−·0001
7	·0000

TABLE V

The Copper Wire No. 24 S.W.G. in N/250 $CuSO_4$ Solution

Load applied (Kilogrammes)	E.M.F. Observed
0	−·003 volt
1	−·0025
2	−·0015
3	−·0002
3·5	+·0010
4	+·0017
4·5	+·0019

TABLE VI

The Copper Wire No. 26 S.W.G. in N/250 $CuSO_4$ Solution

Load applied (Kilogrammes)	E.M.F. Observed
0	−·0040 volt
0·5	−·0031
1	−·0020
1·5	0000
2	+·0017
2·5	+·0020
2·75	+·0020

The constant term E_0 in the Nernst expression $E = E_0 + \frac{RT}{nF} \log c$ has been evaluated by Butler.[2] He puts the constant term E_0 as being equal to $\frac{W_1 - W_2}{nF} + \frac{RT}{nF} \log \frac{A\ N_s}{1000\ N_1 A_1}$ where W_1 is the work required to bring a positive ion from the metallic surface to the equilibrium point, similarly W_2 represents the work required to bring a negative ion from the bulk of the solution to the equilibrium point, $A_1 = V\sqrt{R/n\,W_1}$, $A = \sqrt{R/_2 \pi M}$, M being the gram ion weight, N_1 = number of ions per unit area of the metal surface, N_s = number of ions per c.c. of the salt solution. Other symbols having their usual meanings. Of the two terms occurring in the equation, the first term $\frac{W_1 - W_2}{nF}$ is the only significant one and has a predominant value, the other terms according to Butler (*loc. cit.*) can be left out.

W_1 is the work done in bringing the metallic ion from the surface of the metal to the equilibrium point. Butler (*loc. cit.*) has not taken account of any resistance that would have to be overcome in detaching the metallic ion from the molecular aggregation.

The aggregates of crystals in the metals are of great complexity. When the metals are strained for instance as happens when they are stretched by a load, these aggregates which sometimes are as big as a fraction of a millimetre are altered. Ewing and Rosenhain[3] have made a special study of this fact and find that when a metal is strained beyond the yield point there is a slipping of the crystals as shown in Figs. 3 and 4.

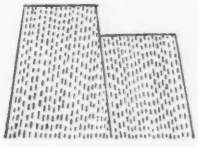

FIG. 3
Before Straining

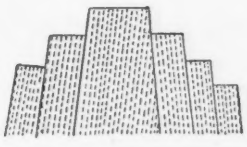

FIG. 4
After Straining

The increase in the positive value of P.D. of the strained wire shows that the tendency for the copper to form ions under stretching strain becomes less as the wieght is increased (Fig. 2) or that the molecular aggregates formed on the surface hinder the formation of ions. This means that the value of W_1 in the case of strained wire is higher than in the case of annealed one.

It is also seen that when the strain is removed the P.D. against the annealed wire does not reach its original value showing that the

molecular aggregates and not the strain itself is responsible for the increase in the potential.

It is very difficult to keep wires free from any strain and therefore the curves have started from different E.M.F.'s although dipping in the same solution shown in Fig. 2.

It is also seen from the graph (Fig. 2) that after a certain load the P.D. becomes constant. This may be due to the fact that at this stage the wire approaches the breaking point and the deformation at the electrode surface is complete.

Conclusion

1. The potential differences of copper wires under stretching strain against annealed wires have been studied.

2. It is found that the strained wire is more positive.

3. It is contended that some work is necessary to detach ions from the metallic surface and is more in the case of strained wire as compared to the annealed one.

REFERENCES

1. Erlanger .. *Ber.*, 1934, **65**, 211-214.
2. J. A. V. Butler .. *Trans. Faraday Soc.*, 1924, **19**, Part III, p. 729.
3. Ewing and Rosenhain .. *Proc. Roy. Soc.*, **45**, p. 85.

CHEMOTHERAPY OF BACTERIAL INFECTIONS

IX. Synthesis of Some Sulphathiazole Derivatives

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Received April 1, 1943

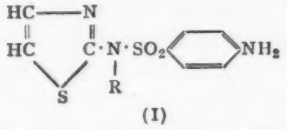
(Communicated by Lt.-Col. S. S. Sokhey, M.A., M.D., I.M.S., F.A.SC.)

Considerable attention is being given in recent times to the discovery of sulphanilamide derivatives for the treatment of infections of the typhoid-cholera-dysentery group. A drug to be ideal for these intestinal infections should, besides possessing very strong bacteriostatic and bactericidal action against the organism concerned, remain localised in the intestine with little of it being absorbed from there into the blood stream. Such a drug should be harmless even with very high concentrations in the intestine because the toxic effects produced by the drugs are mainly the results of their high concentrations in the blood. Basing on this principle, Marshall *et al.*[1] brought forward sulphanilylguanidine as a drug suitable for the treatment of the intestinal infections. Though there are fairly good reports on the treatment of bacilliary dysentery with this drug, it does not impress on us to be as excellent as sulphanilamide or sulphathiazole in their respective spheres of action (compare for example[2]). We attempted therefore to prepare other compounds which may fulfil the criteria mentioned above.

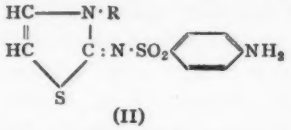
It has previously been reported[3] from this laboratory that sulphathiazole protects mice against septicæmia due to *B. typhosum* and that it shows distinct bacteriostasis against *V. cholerae in vitro* in as low a concentration as 3 mg. per cent., while sulphanilamide even in 10 mg. per cent. shows no bacteriostasis. The disadvantage of this drug for our present purpose is that it is very rapidly absorbed from the intestine so that it is difficult to attain very high concentrations of this in the intestine without increasing correspondingly the concentration in the blood to dangerous limits. So we sought to prepare derivatives of sulphathiazole of such a type that the original therapeutic activity may not be much impaired and at the same time its absorption from the intestine will considerably be reduced. The poor absorption of sulphaguanidine from the intestine which is alkaline in pH, appeared to us to be due to its insolubility in alkali and so we attempted to prepare derivatives of sulphathiazole of formula (I) or (II).

The other object in synthesising compounds of this type is to aid us in correlating chemotherapeutic activity with chemical constitution. Derivatives of sulphathiazole with alkyl substituents at positions 4 and/or 5 of the thiazole ring were previously reported.[4] The compounds described here represent the third possibility of introducing further substituents in the molecule of sulphathiazole.

Sulphathiazole readily condensed with alkyl bromide or iodide (R. Hal) or sulphate in alkaline solution to yield a substitution product wherein the (N^4–) amino group was found to be unsubstituted. The yields were better and the products much purer if the sodium salt of sulphathiazole was treated with the halide in alcohol. While methyl, ethyl, butyl, *iso*amyl and hexyl bromides or iodides readily condensed, *iso*propylbromide was very reluctant to undergo the condensation under these conditions. β-Chloroethylamine and β-bromoethyldiethylamine did condense with sodium sulphathiazole



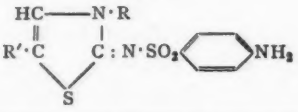
(I)



(II)

but the products obtained could not be crystallised. Ethylchloroacetate as well as ethyl α-chloroacetoacetate on condensation with sodium sulphathiazole yielded the same compound (No. 93); thus the acetyl group in the latter reagent appears to get eliminated in the process. The compounds prepared are listed in the table.

TABLE



Serial No.	R =	R′=	M.P. °C.	Molecular Formula	% Nitrogen	
					Found	Required
83	Methyl-	H	244–46	$C_{10}H_{11}N_3O_2S_2$	15·3	15·6
84	Ethyl-	H	183–85	$C_{11}H_{13}N_3O_2S_2$	15·2	14·8
85	*n*-Butyl-	H	186–88	$C_{13}H_{17}N_3O_2S_2$	13·2	13·5
86	*iso*-Amyl-	H	201– 3	$C_{14}H_{19}N_3O_2S_2$	12·2	12·9
82	*n*-Hexyl-	H	156	$C_{15}H_{21}N_3O_2S_2$	12·4	12·4
106	β-Hydroxyethyl- ..	H	154–56	$C_{11}H_{13}N_3O_3S_2$	13·8	14·0
94	β-Ethoxyethyl-	H	150–52	$C_{13}H_{17}N_3O_3S_2$	1·0	12·0
95	Acetonyl-	H	202	$C_{13}H_{15}N_3O_3S_2$	12·9	13·0
93	Carbethoxymethyl- ..	H	184–85	$C_{13}H_{15}N_3O_4S_2$	12·6	12·3
92	Methyl-	*iso*-Pr	157–60	$C_{13}H_{11}N_3O_2S_2$	13·3	13·0

For the compounds obtained as above described, two structures (I) and (II) are possible. Because of the existence of the triad system, $-N=C-N\cdot R \rightleftharpoons R\cdot N-C=N-$, the compound (I) can easily isomerise to (II) and there are instances known in literature of such an isomerisation. On boiling the alkyl bromides with an alkaline solution of sulphathiazole, a low melting product is first obtained in many cases, which during the process of crystallisation is gradually transformed into one of higher melting point. We have not succeeded in isolating the lower melting ones in these cases (an instance wherein this has been done is reported in the next part) and it is difficult to assert that this is due to isomerisation since dimorphism is also well known among these compounds. After this work was completed, Hartmann and Druey[5] have found that acetsulphanilylchloride condensed with 3-methyl-2-thiazolonimin to yield the same product obtained by methylating acetylsulphathiazole with dimethyl sulphate; this on hydrolysis yielded the methyl derivative (II, R = Me), m.p. 245–6°. On the other hand, *p*-nitrobenzenesulphochloride condensed with 2-methylaminothiazole and the product obtained on reduction yielded a compound, m.p. 109–10°, to be represented as (I, R = Me). Jensen[6] has also reported the same. Druey[7] has recently reported the preparation of a series of compounds of formula (II) by condensing 3-substituted thiazolonimids with *p*-nitrobenzenesulphochloride and reducing the resulting compound and also by condensing (N^4) acctylsulphathiazole with the alkyl halides and hydrolysing the resulting products. The products thus prepared appear to be identical with those reported by us here, though there are slight differences in the melting points (these compounds as a class frequently do not give sharp melting points). Thus we assign the structure (II) to the compounds obtained by us.

The compounds described here, excepting that number 92, have been tested in experimental plague infections in mice during December 1941–January 1942, according to the technique of Sokhey and Dikshit.[8] The methyl derivative 83, showed therapeutic activity comparable to sulphathiazole. The ethyl compound, 84, gave only one survivor out of ten and the average survival time of the mice was slightly greater than that of the controls; so also was the case with the β-hydroxyethyl derivative, 106. All the others were inactive. The methyl derivative, 83, also showed good therapeutic effect in experimental streptococcal and pneumococcal infections in mice. Because of its sparing solubility in water (less than 0·5 mg. per cent.) its *in vitro* bacteriostatic effect could not be studied; however, it is interesting that this compound after oral administration to mice produces sufficient concentration in the blood to exert a pronounced therapeutic effect.

Experimental

Unless otherwise stated, the yields are all to be understood as good in the following experiments.

2-(p-*Aminobenzenesulphonimido*)-3-*methyl thiazolone* (*II*, $R = Me$).—To 2-sulphanilamidothiazole (50 g.) dissolved in sodium hydroxide (2·5 N, 160 c.c.) was added gradually under good shaking dimethyl sulphate (40 c.c.). A crystalline product began to separate. After good shaking it was allowed to stand for about one hour (the solution was distinctly alkaline), then filtered, the crystalline product triturated well with dil. sodium hydroxide, washed well and crystallised from alcohol. Yield, 46 g.

This compound could also be obtained by reacting sulphathiazole in alkaline solution or sodium sulphathiazole in alcohol with methyl iodide. In no case could the low melting isomer be obtained.

This compound was recovered unchanged after boiling with 4 N hydrochloric acid or 2·5 N sodium hydroxide for one hour.

2-(p-*Aminobenzenesulphonimido*)-3-*butylthiazolone* (*II*, $R = Bu$).—Sulphathiazole (12·4 g.) dissolved in sodium hydroxide (2·5 N, 40 c.c.) was boiled with butyl bromide (10 c.c.) or butyl iodide (8 c.c.) till there was no further increase in the quantity of the crystalline solid that separated (about 1 hour). It was cooled, the crystalline solid separated, washed well with alkali, then with water and crystallised from alcohol.

2-(p-*Aminobenzenesulphonimido*)-3-*isoamyl thiazolone* (*II*, $R =$ iso*amyl*).—To sodium salt of sulphathiazole (13·7 g.) was added methyl alcohol (50 c.c.) followed by *iso*amyl bromide (10 c.c.), and the whole heated under reflux for about one hour and then allowed to stand overnight. The crystalline product that separated as such and also from the mother-liquors on dilution, was washed well with dil. alkali, then with water and crystallised from alcohol.

Similarly, the ethyl and hexyl compounds were prepared by utilising ethyl iodide and hexyl bromide.

2-(p-*Aminobenzenesulphonimido*)-3-*carbethoxymethylthiazolone* (*II*, $R = CH_2COOEt$).—Sodium (1·2 g.) was dissolved in absolute alcohol (50 c.c.) and to this was added sulphathiazole (12·8 g.) and the mixture refluxed for 15 minutes. To the solution was added ethyl chloroacetate (8·0 g.) and the refluxing continued for about one hour more. After allowing it to stand overnight the product that had separated was filtered, rapidly washed with alkali, then with water and crystallised from alcohol.

The same compound was obtained when sodium sulphathiazole was condensed with ethyl α-chloroacetoacetate.

2-(p-*Aminobenzenesulphonimido*)-3-*acetonyl thiazolone* (*II*, $R = CH_2CO\,CH_3$).—The sodium salt of sulphathiazole (13·7 g.) was taken up in absolute ethyl alcohol (75 c.c.), chloroacetone (5 g.) was added and the mixture heated under reflux. A crystalline solid soon separated. The mixture was heated for about an hour more when the chloracetone had completely disappeared. It was then filtered, the product washed with alkali, then with water and crystallised from alcohol.

2-(p-*Aminobenzenesulphonimido*)-3-*β-hydroxyethyl thiazolone* (*II*, $R = HO\cdot CH_2CH_2-$).—To sodium salt of sulphathiazole (13·7 g.) in methyl alcohol (20 c.c.) was added ethylene chlorhydrin (10 g.) and the mixture refluxed for about one hour. Further working up of this was as described in the previous cases.

I am indebted to Mr. C. V. Deliwala for the nitrogen estimations recorded here. I also thank Lt.-Col. S. S. Sokhey for his kind interest in these investigations.

Summary

The synthesis of various derivatives of sulphathiazole with alkyl and substituted alkyl substituents at the ring nitrogen of the thiazole nucleus has been described. Of these compounds only the methyl derivative showed good therapeutic activity in experimental streptococcal, pneumococcal and plague infections in mice.

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CHEMOTHERAPY OF BACTERIAL INFECTIONS

X. 2-Acetsulphanilimido-3-acetsulphanilylthiazolone and 2-Diacetsulphanilylamidothiazole. A New Route to Sulphathiazole

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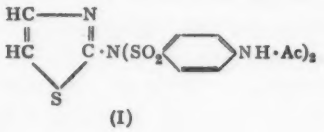
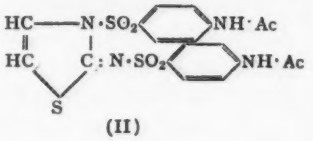
(Communicated by Lt.-Col. S. S. Sokhey, M.A., M.D., I.M.S., F.A.SC.)

When the condensation of 2-aminothiazole and acetsulphanilyl-chloride in molecular proportions is effected in the presence of pyridine, 2-acetsulphanilamidothiazole is produced in good yields. On the other hand, the use of inorganic basic condensing agents in the place of pyridine has now been found to yield different results. Tuda, Iticawa and So[2] have reported that the condensation of acetsulphanilylchloride with 2-aminopyridine in acetone in the presence of sodium bicarbonate yields 2-acetsulphanilamidopyridine ; Bobranski and Eker[2] have obtained the same results by using sodium oxide in the place of sodium bicarbonate. But when the condensation of acetsulphanilylchloride with 2-aminothiazole was effected in the presence of sodium bicarbonate in acetone or aqueous solution, the product obtained was different from the expected 2-acetsulphanilamidothiazole. On crystallisation from alcohol it melted at 128–29°; it was insoluble in alkali but was hydrolysed to sulphathiazole by means of alkali or acid. The same product was obtained by condensing two molecules of acetsulphanilylchloride with one of 2-aminothiazole in pyridine or by the action of acetsulphanilylchloride on an alkaline solution of 2-acetsulphanilamidothiazole. On boiling this product, m.p. 128–29°, with alcohol for some time, it was quantitatively transformed into another, which turned yellow at 190° and charred at 225°. It was also insoluble in alkali and hydrolysed to sulphathiazole. These two compounds can be either dimorphic or isomeric. Though definite evidence against the first possibility has not yet been procured, we are inclined to believe that they are isomers to be represented by the two structures (I) and (II). Since a compound of structure (I) can be



(I)



(II)

expected to isomerise to one of structure (II) and not so easily *vice versa* for the obvious steric reasons, we suggest the structure (I) for the lower melting compound and (II) for the other. Jensen and Thorsteinsson,[3] in a paper which is not accessible and the abstract of which contains no details, have described a compound of structure (II), m.p. 200–220° (turning yellow at 190°); this may quite possibly be identical with the higher melting isomer described here.

It is thus of interest to note that whereas in the presence of pyridine, the condensation of 2-aminothiazole with a molecular equivalent of acetsulphanilylchloride yields 2-acetsulphanilamidothiazole, the use of sodium bicarbonate in the place of pyridine results in the bicondensation product (I) which is easily hydrolysed to sulphathiazole. We have investigated the latter reaction from the practical point of view of the manufacture of sulphathiazole since such a process has not so far been described. We are now satisfied that this is a very feasible method with many practical advantages. The condensation of 2-aminothiazole with two molecular equivalents of acetsulphanilylchloride can be effected in fairly good yields in aqueous suspension in the presence of sodium bicarbonate, calcium or barium carbonate. Calcium carbonate is preferred because of its cheapness and also giving better yields. Another observation made of practical importance is that the yields are better if the solution of aminothiazole is added to the slurry of the sulphochloride. The hydrolysis of the bicondensation product to sulphathiazole proceeds smoothly in good yields. The advantages of this method of preparation of sulphathiazole are: (1) the sulphochloride can be used in the wet state after washing with water by decantation, (2) the use of the costly and now practically unobtainable good grade of pyridine is dispensed with, (3) the products obtained are cleaner and much less coloured and (4) the whole working time is very much shortened. We are engaged in effecting further improvements in this method and studying the reaction with other alky aminothiazoles.

Experimental

2-*Diacetsulphanilylamidothiazole* (I).—(1) To 2-aminothiazole (10 g.) dissolved in dry pyridine (50 c.c.) was added with good shaking crystallised acetsulphanilylchloride (46 g.). After all of it was added, the mixture was warmed on the water-bath for about half an hour, cooled and then poured into cold water. The solid that separated was filtered off, triturated with dilute sodium hydroxide solution, filtered, washed and crystallised from alcohol; yield, 35·0 g. The condensation product obtained in colourless needles melted at 128–29° (Found: N, 11·4; $C_{19}H_{18}N_4O_6S_3$ requires

N, 11·3%). When this product was hydrolysed by boiling for one half hour with about 4 N hydrochloric acid and further worked up as usual, sulphathiazole was obtained in very good yields.

(2) To a solution of 2-acetsulphanilamidothiazole (7·2 g.) in sodium hydroxide (60 c.c. of 2·5 N) was added with cooling and good shaking finely powdered acetsulphanilylchloride (6·0 g.). The whole was kept well ground in a mortar and the solution maintained slightly alkaline if necessary by addition of alkali. After allowing to stand for some hours, the product was filtered off, washed with water and crystallised from alcohol; m.p. 127–29° (mixed m.p. with the foregoing sample being the same). Yield, about 10 g.

(3) The same product was obtained on condensing 2-aminothiazole with one or two molecular equivalents of acetsulphanilchloride in aqueous solution in cold in the presence of 2·5 molecular equivalents of sodium bicarbonate.

2-*Acetsulphanilimido*-3-*acetsulphanilylthiazolone* (II).—When the product, m.p. 127°–29°, was boiled in alcohol for one to two hours, it was transformed into one of higher melting point; this product which is sparingly soluble in alcohol, after repeated crystallisations from alcohol, was obtained in colourless needles which turns yellow at 190° and charrs at 225° (Found: N, 11·3; $C_{10}H_{10}N_4O_6S_3$ requires N, 11·3%).

Preparation of Sulphathiazole.—The acetsulphanilylchloride prepared from acetanilide (1·0 kg.) and commercial chlorosulphonic acid (2·4 l.), was washed free from acid with water and suspended in water (8 to 10 l.). In case the solution was acidic, it was neutralised with calcium carbonate and then a further quantity of calcium carbonate (500 g.) was added and stirred well. A solution of crude 2-aminothiazole (250 g.) in water (4 l.) was slowly run in with good stirring. There was a vigorous evolution of carbon dioxide and the stirring was continued till it practically subsided. After allowing it to stand overnight, the solid was filtered off, triturated with dilute hydrochloric acid to decompose the excess of calcium carbonate and then washed with water (a sample of the condensation product on crystallisation from ethyl alcohol had m.p. 128–29°). The solid obtained was hydrolysed as usual by boiling with about 5 N hydrochloric acid or about ten per cent. sodium hydroxide. On neutralising the filtrate, sulphathiazole was thrown out. This was collected and recrystallised from boiling water (charcoal). The yield of the product obtained in colourless needles was about 250 g. and this can doubtless be improved.

We thank Lt.-Col. S. S. Sokhey, Director, for his keen interest in these investigations.

Summary

2-Aminothiazole condensed with acetsulphanilylchloride in aqueous solution or suspension in the presence of sodium bicarbonate, calcium carbonate or barium carbonate to yield 2-diacetsulphanilylamidothiazole, m.p. 128–29°; the same product is also obtained by condensing 2-aminothiazole with two molecular equivalents of acetsulphanilylchloride in pyridine or by condensing 2-acetsulphanilamidothiazole with acetsulphanilylchloride in alkaline solution. This compound on boiling with alcohol isomerises into 2-acetsulphanilimido-3-sulphanilylthiazolone. These two products are hydrolysed by acid or alkali to sulphathiazole in good yield. A process of preparation of sulphathiazole is described.

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FLUORESCENCE REACTIONS WITH BORIC ACID AND *o*-HYDROXY-CARBONYL COMPOUNDS, AND THEIR APPLICATION IN ANALYTICAL CHEMISTRY

Part II. Detection of —C(OH)—C—C(=O)— in Aromatic Compounds containing C, H and O only

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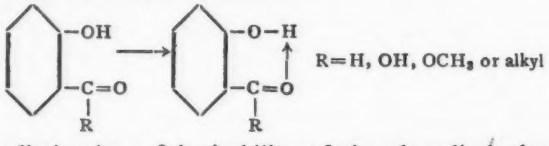
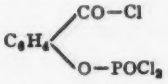
It is well known that a hydroxyl ortho to the carbonyl group in aromatic compounds, —C(OH)—C—C(=O)—, exhibits certain peculiarities, *viz.*, that it is not readily methylated and that it is less phenolic than when it is present in other positions. This behaviour has been observed not only with the simpler compounds such as resacetophenone, salicylic acid, etc., but also with the hydroxy-flavones, -flavonols, -flavanones, -chromones, -chalkones, -xanthones, and -anthraquinones containing this group. These peculiarities have been ascribed to the existence of chelation between the hydroxyl hydrogen and the carbonyl oxygen thus:



leading to a diminution of ionisability of the phenolic hydrogen atom and also causing fixation of the double bonds. When the hydroxyl is in the meta or the para position to the carbonyl it behaves in the normal manner. Consequently the qualitative detection of the presence of a hydroxyl ortho to the carbonyl group is of considerable interest.

No attempt seems to have been made in the past to develop a general reaction for the detection of this group in various types of compounds. However, a few reactions which distinguish ortho-hydroxy carbonyl compounds from the meta- and para-compounds have been recorded and these could be utilised, though to a limited extent for this purpose.

Anschütz[1] found that while the, *o*-, *m*-, and *p*-hydroxy benzoic acids themselves reacted with phosphorous pentachloride yielding the phosphorous oxychloride derivative of the phenolic carboxylic acid chloride of the following type:

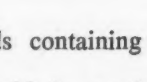


ortho-hydroxybenzoic acids in which the second ortho position to the hydroxyl is already occupied give the free acid chlorides. Obviously, the reaction is of no value for detecting the presence of the ortho-hydroxy-carbonyl group in the simple unsubstituted hydroxy-benzoic acids. However, it could be employed, for example, with *o*-cresol-carboxylic acids.

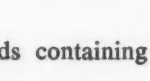
Jean-Renaud[2] found that only esters of *o*-hydroxybenzoic acids yield with hydroxylamine and alkali in aqueous solution the corresponding hydroxamic acids, R-CO-NHOH, while the *m*- and *p*-compounds do not. Since the hydroxamic acids can be readily detected by means of the characteristic property which they possess of yielding a red or violet colour with ferric chloride, this difference could be utilised to distinguish the three types of hydroxy acids. However, it fails with the ester of β-naphthol-β-carboxylic acid, and Angelli and Castellana[3] showed that if an alcoholic solution is employed, the ester of *m*-hydroxybenzoic acid also gives the hydroxamic acid. In this connection it is of interest to note that among the unsubstituted *o*-, *m*-, and *p*-hydroxybenzoic acids the ortho acid can be easily and directly distinguished by means of its colour reaction with ferric chloride. While the ortho compound yields a violet colour, the *m*-, and *p*-compounds give none. It may, however, be pointed out that substitution brings about a marked change in the colour obtained with the ferric chloride as, for example, in the case of 5-nitro-salicylic acid which yields a red colour and hence the ferric chloride colour reaction is not a sure test for the *o*-hydroxybenzoic acids.

A third reaction distinguishing the *o*-hydroxy-carboxylic acids from the *m*-, and *p*-acids has been reported by Nölting.[4] Anilides of the ortho acids on treatment with dimethylaniline and phosphorous oxychloride yield compounds of the malachite green series whereas those of the *m*- and *p*-compounds yield derivatives of dialkyl-amido-benzophenones.

With regard to the hydroxy-ketones Pfeiffer *et. al.*[5] found that while carbonyl compounds and *m*- and *p*-hydroxy-carbonyl compounds yielded with stannic chloride additive compounds, in the presence of an ortho-hydroxyl internally complex (chelate) compounds were obtained. The latter compounds are closely related to the tin lakes and are coloured unlike the additive compounds.

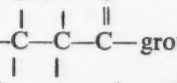
In the group of the hydroxy-anthraquinones, Dimroth *et al.*[6] found that the α-hydroxy compounds containing the  group gave on treatment with boracetic acid in acetic anhydride solution characteristic colour changes, in many cases with fluorescence, due to the formation of boracetate complexes (chelation) involving the hydroxyl and carbonyl and that when the hydroxyl was not in the ortho position to the carbonyl only acetylation of the former occurred. Brass *et al.*[7] utilised this reaction for proving the absence of *l*-hydroxyl in the dihydroxyphenanthraquinone (2 : 4) they had prepared.

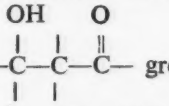
Feigl and Krumholz[8] observed that boric acid itself reacts with α-hydroxy-anthraquinones dissolved in concentrated sulphuric acid yielding characteristic colour changes which can be used either for the detection of boric acid or the α-hydroxyanthraquinones. These authors explained these colour changes as due to the formation of inner complex (chelate) boric esters or of similar boric-sulphuric acid esters involving the ortho hydroxyl and the carbonyl group. From the data given by Meyer[9] it is clear that generally in the absence of a hydroxyl ortho to the carbonyl group, no prominent colour changes occur on the addition of boric acid. However, a few exceptions are known. 2 : 3-dihydroxy-anthraquinone gives a colour change, though not a prominent one (red-brown to brown) on adding boric acid, but it does not contain a hydroxyl ortho (α) to the carbonyl group, while 1 : 3-dihydroxy- and 1 : 4 : 5 : 8-tetrahydroxy-anthraquinones fail to give a colour change on adding boric acid though they contain the α-hydroxyl.

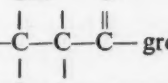
Rangaswami and Seshadri[10] showed that Wilson's boric-citric acid colour test is quite useful for the detection of the presence of a 5-hydroxyl in hydroxy-flavones and -flavonols and that a positive reaction is given by the methyl ethers also. Similar results were obtained with the *o*-hydroxy-chalkones and their methyl ethers. However, the 5-hydroxy-flavanones, naringenin and hesperetin, and the simpler *o*-hydroxy compounds, salicylic acid and resacetophenone fail to give the test. These authors pointed out that for a compound to yield a positive reaction the molecule should contain: (1) a keto-group, (2) an ortho hydroxyl or methoxyl and (3) an external double bond in conjugation with the C=O. This reaction is obviously limited to those compounds containing the  group in which there is present in addition an external double bond in conjugation with the

C = O as in the case of 5-hydroxy-flavones, -flavonols and the 2-hydroxy-chalkones.

To the above may be added the ferric chloride colour reactions for the *o*-hydroxy-carbonyl compounds, acids, aldehydes and ketones which serve to a limited extent to distinguish the *o*- from the *m*- and *p*-compounds.

It is clear from the above that the available reactions for the detection of the  group have been developed with reference to particular types of compounds and have consequently a limited range of applicability.

In a previous communication[11] which may be regarded as Part I of this series, Neelakantam and Row reported that addition of boric acid to solutions of the *O*-hydroxy-carbonyl compounds in concentrated sulphuric acid, except in a few cases, brought about either a marked intensification or a change in colour of the fluorescence exhibited by them in daylight or under the ultra-violet lamp. In some cases fluorescence appeared only on the addition of boric acid, the solutions (H_2SO_4) of the compounds themselves being non-fluorescent. These results were given not only by the simpler compounds such as salicylic acid, resacetophenone, etc., but also by most of the 5-hydroxy-flavones, -flavonols and -flavanones examined. In the absence of the  group no fluorescence effects (*loc. cit.*) were observed except in one case (3:7-dihydroxy-flavone). These authors suggested that the reaction might serve for the detection of this group. It was, however, pointed out by them that a negative result does not necessarily indicates the absence of this group.

Since the previous work was published several other *o*-hydroxy-carbonyl compounds became available as a result of synthetic work done in our laboratories and it was felt desirable to examine the scope of this fluorescence reaction as a general reaction for the detection of the  group in aromatic compounds. The present investigation is confined to compounds containing carbon, hydrogen and oxygen only. Feigl (*loc. cit.*) examined the colour reactions of the α-hydroxyanthraquinones with boric acid in daylight only and hence the few available compounds of this series were included in the present investigation. In all twenty-six compounds including some

o-hydroxychalkones recently synthesised in our laboratory have now been examined. Further, a variety of aromatic compounds containing the hydroxyl and carbonyl groups in other than the ortho position to each other and also those in which the hydroxyl or the carbonyl is absent have been examined to elucidate the limitations of the reaction.

Experimental

Solutions.—The boric acid solution and the solutions of the substances under investigation were prepared as described already.[11]

Procedure.—The procedure adopted was also identical with the one previously described.

Results.—The colour of the fluorescence obtained with the *o*-hydroxy-carbonyl compounds is recorded below. The results obtained with compounds in which the two groups are not ortho to each other and also those in which one of them is absent are also recorded in order to test the specific nature of the reactions.

o-Hydroxy-ketones.—2-Hydroxy-6-methoxy-acetophenone gave a bright yellow and 2-hydroxy-4: 6-dimethoxy-acetophenone a greenish yellow fluorescence with boric acid under the lamp. 2-Hydroxy-3: 6-dimethoxy-acetophenone and *ω*-methoxy-phloracetophenone gave no fluorescence with boric acid even under the lamp. With all these compounds the blanks exhibited no fluorescence either in daylight or under the lamp.

o-Hydroxy-aldehydes.—2 : 4-Dihydroxy-6-methyl-benzaldehyde gave a bright greenish yellow and 2-hydroxy-4-methoxy-6-methyl-benzaldehyde a greenish yellow fluorescence with boric acid under the lamp. With the two compounds no fluorescence was obtained either in daylight or under the lamp in the blank test. 2-Hydroxy-4: 6-dimethoxy-benzaldehyde, however, gave a pale yellow fluorescence in the blank test and a deeper yellow fluorescence with boric acid under the lamp.

o-*Hydroxy-carboxylic acids and esters.*—Atranorin and ethyl rhizonate gave no fluorescence in the blank test but with boric acid they gave a pale blue fluorescence under the lamp. Montagnetol and lecanoric acid gave a pale violet fluorescence under the lamp even without boric acid and on its addition this became deeper in both cases. The methyl ester of karanjic acid gave a pale blue fluorescence in the blank and a deeper blue with boric acid under the lamp.

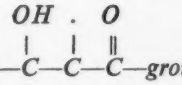
o-*Hydroxy-chalkones.*—2 : 4 : 3′ : 4′—Tetrahydroxy-chalkone (butein) dissolved in sulphuric acid gave a green fluorescence visible in daylight itself and on treatment with boric acid, there was appreciable increase in its intensity; the blank appeared greenish yellow under the lamp and with boric

acid a deeper greenish yellow. 2:4-Dihydroxy-chalkone gave a pale greenish yellow fluorescence in the blank and a deeper greenish yellow with boric acid under the lamp. 2:4:4′-Trihydroxy-3′-methoxy-chalkone gave an yellow fluorescence with boric acid under the lamp and none without it; in daylight no fluorescence was obtained with or without boric acid.

The following chalkones recently synthesised by Seshadri *et al.* (unpublished work) gave no fluorescence with or without boric acid in daylight or under the lamp :—

2:6-Dihydroxy-, 2:4′-dihydroxy-6:3′-dimethoxy-, 2:5:4′-trihydroxy-6:3′-dimethoxy-, 2-hydroxy-3:6-dimethoxy-, 2-hydroxy-3:6:4′-trimethoxy-, 2:4′-dihydroxy-3:6:3′-trimethoxy-, and 2-hydroxy-5 : 6 : 3′ : 4′-tetramethoxy-chalkones.

α-*Hydroxy-anthraquinones.*—Quinizarin gave a pale yellow fluorescence in daylight itself without any boric acid and on its addition it was deepened; there was no appreciable colour change with the boric acid. The blank gave an orange-yellow fluorescence under the lamp and with boric acid this became deeper yellow. Alizarin, quinalizarin and *rheum*-emodin (2-methyl-4:5:7-trihydroxy-anthraquinone) gave no fluorescence with or without boric acid in daylight or under the lamp. In these cases prominent colour changes occurred on the addition of boric acid. Alizarin gave a pale pink solution which became violet on adding boric acid, with quinalizarin the change was from violet to blue and in the case of *rheum*-emodin from orange to violet-red.

Compounds in which the  *group is absent.*—The following compounds gave no fluorescence with or without boric acid in daylight or under the lamp :—

p-Hydroxy-benzaldehyde, vanillin, isovanillin, protocatechuic aldehyde, benzoin, benzil, α-naphthol, 5:6:3′:4′-tetramethoxy-flavanone, anisic acid and gallic acid.

In the following cases the solutions of the substances in concentrated sulphuric acid gave fluorescence under the lamp but on the addition of boric acid there was no change in intensity or in colour:—

m-, and *p*-Hydoxy-benzoic acids, mandelic acid, benzophenone, phthalic acid, β-naphthol and 3-methoxy-7-hydroxy-8-methyl-flavone.

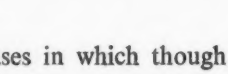
Other compounds examined for negative evidence were the following:—

Benzilic acid, umbelliferone, 4-methyl-, 5-methyl-, 4:8-dimethyl-, and 8-allyl-umbelliferone; 2-methyl-3-methoxy-7-hydroxy-, and 2-methyl-3-

methoxy-7-allyloxy-chromone, and 6: 8-diallyl-7-hydroxy-flavone. All these gave fluorescence when dissolved in sulphuric acid even in daylight but addition of boric acid produced no change.

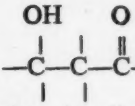
7-Methoxy-3-hydroxy-flavone, however, behaved in an exceptional manner. Its solution in concentrated sulphuric acid exhibited a light greenish blue fluorescence in daylight which on the addition of boric acid became a bright blue; under the lamp it was bright green in the blank and deep blue with boric acid.

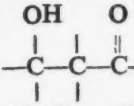
Discussion

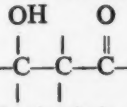
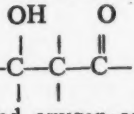
In the case of the *o*-hydroxy-ketones, -aldehydes, and -acids, the results now obtained generally support the conclusions reported in the previous communication (*loc. cit.*). Among the compounds now examined also there are a few cases in which though the  group is present negative results are obtained. Among the simpler *o*-hydroxy-carbonyl compounds it appears that when the 3-position is occupied either by a methyl or a methoxy group as in 3-methylresacetophenone, 2-hydroxy-3: 6-dimethoxy acetophenone and 3-methyl-4-methoxy-2-hydroxybenzoic acid, no fluorescence is observed with boric acid either in daylight or under the lamp. *ω*-Methoxy-phloracetophenone also gives a negative result with boric acid.

In the group of the *o*-hydroxy-chalkones, out of the ten cases examined positive fluorescence effects were obtained only with three and it is interesting to note that all these are derived from *β*-resacetophenone. A comparison of the results obtained with the chalkones and the corresponding ketones shows that the behaviour of the two classes is not always parallel and while the ketones may exhibit the fluorescence effects the corresponding chalkones may not. Thus *γ*-resacetophenone itself yields positive results while the chalkones derived from it do not but 2-hydroxy-3 : 6-dimethoxy-acetophenone itself gives negative results and so also the chalkones derived from it. It may be stated in general that conversion of a ketone to a chalkone reduces the capacity to exhibit fluorescence.

The *α*-hydroxy-anthraquinones yield strongly coloured solutions when dissolved in concentrated sulphuric acid and even when diluted largely with the acid they do not give any fluorescence effects with boric acid except in the case of quinizarin. It appears that when addition of boric acid produces colour changes, no fluorescence effects are obtained.

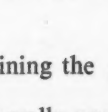
Compounds which do not contain the  —group gave negative results with boric acid, with one exception, in all the cases examined.

The results presented in this paper in conjunction with those already reported in Part I (*loc. cit.*) show clearly that a large number of compounds containing the  —group such as the *o*-hydroxy-acids, -ketones and -aldehydes; the 5-hydroxy-flavones, -flavonols and -flavanones; *o*-hydroxy-chalkones and α-hydroxy-anthraquinones give positive fluorescence effects with boric acid. However, there are cases in which though this group is present negative results are obtained. With the data available at present no general explanation could be given for these exceptions.

Among the compounds examined so far only in the cases of 3: 7-dihydroxy-flavone reported in Part I and 7-methoxy-3-hydroxy-flavone in the present paper were fluorescence effects obtained with boric acid in the absence of the  group. It is of interest to note in this connection that in the boric-citric acid test also both compounds gave a deep blue fluorescence but no colour.[10] 7-Hydroxy-flavone itself gives a negative result in the fluorescence as well as in the boric-citric acid test. Obviously, therefore, the 3-hydroxyl group in 3: 7-dihydroxy-flavone and in its 7-methyl ether is responsible for their exceptional behaviour in the fluorescence test. From the data available, therefore, it could be deduced that, with these two exceptions, a positive result with boric acid indicates the presence of the  group in aromatic compounds containing carbon, hydrogen and oxygen only but the converse is not true.

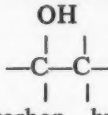
It is evident that this reaction is of greater applicability than any so far reported in the literature. It is much more general than the others and is not confined to any one type of compounds. Further the test is very easily carried out and it does not involve further substitution as in Anschütz's method or preparation of derivatives as in Jean-Renaud's and Nölting's methods.

Conclusion

1. Addition of boric acid to aromatic compounds (C, H, and O only) of various types containing the group  , dissolved in concentrated sulphuric acid generally produces a marked intensification or a change in colour of the fluorescence exhibited by them in daylight or under the lamp. In several cases the solution of the compound in sulphuric acid is itself non-fluorescent and fluorescence appears on adding boric acid.

2. In a few cases even when this group is present no fluorescence effects are obtained with boric acid.

3. 3:7-Dihydroxy-flavone and its 7-methyl ether are exceptions in that they give positive reactions with boric acid even though the above group is absent.

4. The fluorescence effects obtained with boric acid could be utilised for the detection of the  group in various types of aromatic compounds containing carbon, hydrogen and oxygen only. A positive reaction indicates the presence of this group but the converse is not true.

5. This reaction is more general than all the others described in literature and is also easily carried out.

Further work is in progress.

The authors wish to express their thanks to Prof. T. R. Seshadri for valuable help rendered in the course of this investigation.

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THE PHOTO-REDUCTION OF FERRIC CHLORIDE IN PRESENCE OF AQUEOUS ACETONE AND ANHYDROUS ETHER

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Although it is known that in admixed solutions with acetone ferric chloride is reduced in light (1) no work of a quantitative nature has yet been reported in literature. Some work, however, has been done on the photo-reduction of ethereal solutions of ferric chloride, but it lacks in thoroughness of treatment. Observations of a purely qualitative nature were made by Benrath (2), Puxeddu (3) and Spcier (4) using different regions of radiations as source of light. Later on, a quantitative study of the reaction was made by Puxeddu and Vodret (5) in sunlight as well as in arc light, but the method employed by them to estimate the amount of reduction is open to objection. They found that the reaction is of the first order and is completed in one hour. Further they found that the nature of the incident light has a marked effect on the reaction; at the same temperature the decomposition is much slower in arc light than in sunlight.

Talpade (6) has recently critically examined the applicability of various analytical reagents to estimate small quantities of ferrous iron in presence of large amounts of ferric iron and organic substance and has come to the conclusion that ceric sulphate is the only reagent which can be best employed for an unambiguous and direct measurement of a high degree of accuracy. The present investigation was therefore undertaken mainly with a view to obtain accurate quantitative data on the kinetics of the photo-reduction of ferric chloride in presence of aqueous acetone and anhydrous ether using ceric sulphate method for the estimation of the amount of reduction from time to time. The various effects on the reaction due to the changes in the concentration of ferric chloride, temperature, wave-length and the intensity of light have been studied and the quantum efficiency of the reactions has been also measured in light of different spectral regions at different temperatures with different concentrations of ferric chloride solutions.

Experimental

The source of light was a Phillip's 1000-watt vertical type cinema projector lamp worked at a constant current of 4·2 amps. The reaction cell

was made of optically plane parallel quartz plates; its capacity was 4·5 c.c. and internal thickness 5 mm. It was cemented at the top to a thick glass plate with two holes through which passed siphon tubes ground to the holes in the plate. To the siphon tubes were attached pieces of India rubber tubing which were closed air tight.

The light filters were Kodak's wratten filters. The mean wave-length transmitted in each case was determined spectroscopically and was found to be as follows:—

Blue filter	..	.. 4725 A.U.
Yellow filter	..	.. 5975 A.U.
Red filter	..	.. 6625 A.U.

Ferric chloride used was of A.R. quality obtained from B.D.H. It was dissolved in redistilled water with the addition of a certain amount of HCl in order to prevent the hydrolysis of ferric chloride (7) and also to stabilise the pH. Ethereal solutions of ferric chloride were prepared in Merck's extra-pure ether. Aqueous solutions of acetone were made by dissolving Merck's extra-pure quality acetone in redistilled water. These solutions were made in the dark and stored in air tight bottles which were always kept in a cool dry place.

After the elimination of heat radiations the parallel beam of light was incident on the reaction cell which was carefully screened from other radiations and was shaken from time to time to avoid the formation of "inner filters" (7). A Hilger thermopile connected to a Moll galvanometer recorded the intensity of the incident and the emergent beam of light. The absorbed energy was calculated from the galvanometer deflection differences for the reacting solution with and without ferric chloride, which were calibrated in terms of Hefner 100.

After insolating the mixture for a certain known interval, the cell was taken out of the thermostat and connected to a titration bottle and a wash bottle. On exhausting the air in the titration bottle the water from the wash bottle passed through the reaction cell to the titration bottle, thus draining the cell completely of its contents. The amount of reduction was determined by titrating the mixture against a standard solution of ceric sulphate with diphenylamine in sulphuric acid as an internal indicator in the presence of a few c.c. of syrupy phosphoric acid.

The results obtained are given in the following tables in which

a = the initial concentration of ferric chloride expressed in millimoles in 4 c.c. of the reaction mixture,

b = the initial concentration of acetone expresesd in millimoles in 4 c.c. of the reaction mixture,

T = the temperature at which the reaction is studied,

I = the incident intensity in terms of galvanometer deflections,

λ = the wave-length of the exciting radiations in A.U.,

X = the amount of reduction of ferric chloride in millimoles in 4 c.c. of the reaction mixture,

t = the time of exposure in minutes, and

K = the unimolecular velocity constant.

TABLE I

Ferric Chloride and Aqueous Acetone

$b = 0{\cdot}2764$; T = 35°.

t	$a = 0{\cdot}8604$		$a = 0{\cdot}5736$		$a = 0{\cdot}2868$	
	X×10³	K×10⁴	X×10³	K×10⁴	X×10³	K×10⁴
60	6·12	1·151	4·05	1·190	2·12	1·228
120	12·06	1·170	7·96	1·190	4·18	1·247
180	17·86	1·164	11·88	1·177	6·26	1·228
240	23·58	1·161	15·88	1·180	8·28	1·228
300	29·36	1·159	19·66	1·174	10·26	1·220
360	35·19	1·158	23·49	1·164	12·24	1·209
480	46·44	1·156	31·18	1·171	16·06	1·204
600	57·60	1·155	38·70	1·170	19·80	1·194

TABLE II

Ferric Chloride and Anhydrous Ether

T = 35°

t	$a = 0{\cdot}9583$		$a = 0{\cdot}4863$		$a = 0{\cdot}2448$	
	X×10³	K×10⁴	X×10³	K×10⁴	X×10³	K×10⁴
60	7·92	1·381	4·14	1·420	2·34	1·573
120	15·84	1·381	8·28	1·439	4·64	1·573
180	23·54	1·381	12·33	1·420	6·84	1·561
240	31·14	1·372	16·29	1·420	9·04	1·554
300	38·52	1·366	20·16	1·412	11·12	1·543
360	45·99	1·369	24·12	1·414	13·23	1·541
480	60·93	1·367	31·86	1·410	17·46	1·545
600	75·60	1·370	39·60	1·416	21·60	1·539

It can be seen from the above tables that the photo-reduction of ferric chloride in the presence of acetone and ether is not a zeromolecular reaction because the values of X/t decrease steadily as the reaction proceeds. If the reaction is of the first order, then the time required for the completion of the same fraction of the reaction carried out with different initial concentrations should be the same. Different values of X/a for reactions started with different initial concentrations were therefore calculated and are given in the following table:

TABLE III

t	X/a for acetone			X/a for ether		
	$a = 0{\cdot}8604$	0·5736	0·2868	0·9583	0·4863	0·2448
60	0·0071	0·0071	0·0074	0·008	0·009	0·010
120	0·0140	0·0139	0·0146	0·016	0·017	0·019
180	0·0208	0·0207	0·0218	0·025	0·025	0·028
240	0·0274	0·0277	0·0289	0·032	0·034	0·037
300	0·0341	0·0343	0·0358	0·040	0·042	0·045
360	0·0409	0·0410	0·0427	0·048	0·050	0·054
480	0·0540	0·0544	0·0560	0·064	0·066	0·071
600	0·0669	0·0675	0·0690	0·079	0·081	0·088

It will be seen from the above table that for the same period of insolation the values of X/a are very nearly independent of the initial concentration of ferric chloride. The photo-reduction of ferric chloride in presence of acetone and ether, therefore, is a unimolecular reaction. This is confirmed by the facts that (*i*) the plot of log (a-X) against the time of insolation is a straight line, in all cases, and (ii) the values of the unimolecular velocity constants, given in Tables I and II, agree fairly well for a particular concentration of ferric chloride.

The mean values of the velocity constant for different initial concentrations of ferric chloride are given in the following table:

TABLE IV

	Acetone			Ether		
a	0·8604	0·5736	0·2868	0·9583	0·4863	0·2448
$K \times 10^4$	1·159	1·177	1·220	1·373	1·419	1·554
		Mean →	1·185		Mean →	1·449

It will be seen from the above table that the velocity constant decreases with increase in the concentration of ferric chloride, the deviations from the mean being beyond the experimental error.

The effect of temperature

The effect of temperature was examined by studying the kinetics of the reaction at 30° and 40° in addition to that studied at 35° in composite light. The results obtained are given in the following tables:

TABLE V

Ferric Chloride and Acetone

t	$a = 0{\cdot}8604$		$a = 0{\cdot}5736$		$a = 0{\cdot}2868$	
	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$
			Temperature 30°			
60	5·40	1·036	3·42	0·998	1·94	1·113
120	10·71	1·036	6·72	0·998	3·74	1·074
180	15·75	1·023	9·99	0·985	5·40	1·062
240	20·97	1·027	13·27	0·988	7·16	1·065
			Temperature 40°			
60	6·93	1·343	4·54	1·343	2·43	1·420
120	13·77	1·343	8·82	1·305	4·72	1·381
180	20·52	1·330	13·14	1·292	6·93	1·356
240	27·00	1·333	17·46	1·295	9·18	1·363

TABLE VI

Ferric Chloride in Ether

t	$a = 0{\cdot}9583$		$a = 0{\cdot}4863$		$a = 0{\cdot}2448$	
	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$
			Temperature 30°			
60	7·34	1·266	3·92	1·343	2·15	1·458
120	14·49	1·266	7·52	1·305	4·23	1·439
180	21·51	1·253	11·25	1·292	6·21	1·420
240	28·35	1·257	14·85	1·295	8·19	1·420
			Temperature 40°			
60	9·72	1·688	5·13	1·765	2·94	1·995
120	19·26	1·688	10·12	1·746	5·74	1·957
180	28·71	1·688	15·12	1·752	8·46	1·957
240	37·98	1·688	20·07	1·756	11·16	1·948

The effect of temperature on the velocity of the reaction is quite appreciable as will be seen from the following table which gives the mean values of the unimolecular velocity constants:

TABLE VII

t	Mean values of $K \times 10^4$ for					
	Acetone			Ether		
	$a = 0{\cdot}9604$	0·5736	0·2868	0·9583	0·4863	0·2448
30°	1·030	0·992	1·078	1·260	1·309	1·434
35°	1·162	1·184	1·233	1·379	1·425	1·565
40°	1·337	1·309	1·380	1·688	1·755	1·964

The values of temperature coefficient between different temperatures have been calculated and they are given in the following table:

TABLE VIII

Temp. coeff. bet. temps.	Acetone			Ether		
	$a = 0{\cdot}8604$	0·5736	0·2868	0·9583	0·4863	0·2448
30°–35°	1·128	1·193	1·144	1·094	1·089	1·091
35°–40°	1·150	1·105	1·119	1·224	1·231	1·225
30°–40°	1·298	1·319	1·280	1·340	1·341	1·370

It can be seen from the above table that the values of the temperature coefficient are almost constant within limits of experimental error and are practically independent of the initial concentration of ferric chloride. Also it will be seen in the case of ether that the temperature coefficient is a function of the temperatures between which it is calculated.

The low values of the temperature coefficient obtained in both the cases indicate that the photo-reduction of ferric chloride in presence of ether and acetone may be considered as a truly photochemical reaction.

The effect of wave-length

The effect of different wave-lengths was examined by studying the kinetics of the reaction in radiations filtered through the three filters described before. The results obtained are given in the following tables:

TABLE IX

Ferric Chloride and Acetone

$a = 0{\cdot}9870$; $b = 0{\cdot}2764$; $T = 35°$

t	Blue filter		Yellow filter		Red filter	
	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$
60	0·92	1·535	0·72	1·190	0·63	1·074
120	1·80	1·535	1·42	1·190	1·25	1·055
180	2·67	1·522	2·08	1·177	1·86	1·049
240	3·55	1·526	2·75	1·180	2·47	1·055

TABLE X

Ferric Chloride and Ether

$a = 0{\cdot}9583$; $T = 35°$

t	Blue filter		Yellow filter		Red filter	
	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$
60	0·99	1·727	0·81	1·420	0·69	1·190
120	1·96	1·727	1·60	1·401	1·36	1·190
180	2·89	1·702	2·38	1·407	2·02	1·190
240	3·84	1·708	3·16	1·401	2·66	1·180

It can be seen from the above tables that the effect of the wave-length of the incident radiations on the velocity constant is quite marked. This has been brought out in the following table which gives the values of the unimolecular constant, taken from the above tables:

TABLE XI

Filter	$K \times 10^4$ for	
	Acetone	Ether
Blue ..	1·530	1·716
Yellow ..	1·184	1·407
Red ..	1·058	1·188

TABLE XII

I	Acetone ($a = 0{\cdot}972$)		Ether ($a = 0{\cdot}9583$)	
	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$
25·00	7·38	1·266	8·64	1·496
21·15	6·12	1·074	7·20	1·266
14·45	4·32	0·767	4·86	0·844

It will be seen that the values of the velocity constants in the three frequencies used decrease in the order blue > yellow > red, that is, the reaction takes place the most in blue light and the least in red. These results are as expected since the total energy of the absorbed light increases with the increase in the frequency of the exciting radiations.

The effect of intensity

The effect of the intensity of the incident light was examined by studying the reaction for one hour in composite light at 35°. The changes in the incident intensity were effected by changing the distance of the source of light from the reaction cell, thereby causing no change in the quality of the light. The results obtained are given in Table XII.

It will be seen that the effect of the intensity of the incident light is quite marked, the velocity constant is increased on increasing the intensity. The following table gives the ratios of the velocity constants and the corresponding ratios of the intensities, in which I_1, I_2 and I_3 are the intensities and K_1, K_2 and K_3 the corresponding values of the velocity constants:

TABLE XIII

		Acetone	Ether
$I_2/I_1 = 1{\cdot}46$	$K_2/K_1 =$	1·40	1·50
$I_3/I_2 = 1{\cdot}18$	$K_3/K_2 =$	1·18	1·18
$I_3/I_1 = 1{\cdot}73$	$K_3/K_1 =$	1·65	1·77

It can be seen from the above table that the rate of reaction is directly proportional to the intensity of the incident light, the slight deviations being within the limits of experimental error. As the amount of absorbed radiation is directly proportional to the incident intensity (*cf.* Dhar, "The Chemical Action of Light"), these results show that the rate of reaction is directly proportional to the absorbed energy.

Quantum efficiency measurements

The quantum efficiency with different concentrations of ferric chloride for different wave-lengths was measured by using the same filters as used in the study of the kinetics of the reaction. The time of exposure of the reaction mixtures was one hour for all the measuremants. The number of molecules changed during the period of exposure was calculated from the titration data and the number of quanta absorbed was determined from the measurement of the absorbed energy. The results obtained are given below:

TABLE XIV

Organic compound	*a*	Quantum efficiency at 35° for		
		4725 A.U.	5975 A.U.	6625 A.U.
Acetone	0·50	0·24	0·20	0·16
	0·10	0·38	0·30	0·24
	0·05	0·41	0·32	0·26
Ether	0·48	0·52	0·42	0·34
	0·12	0·76	0·61	0·49
	0·06	0·82	0·66	0·53

It will be seen from the above table that the values of the quantum yield in case of acetone are low, being in all cases less than 0·5; in ethereal solutions of ferric chloride, however, the yields are much higher. Further in will be seen that the quantum efficiency increases with dilution; the increase is fairly large on decreasing the concentration from 0·5 to 0·1 but is comparatively much less when it is decreased from 0·1 to 0·05. Also it can be seen that the values of the quantum yield decrease as the wave-length of the exciting radiation is increased. It is evident, therefore, that more molecules of ferric chloride are changed for every quantum of light absorbed, in light of a higher frequency that in that of a lower one.

The effect of temperature on the quantum yield was examined by determining the quantum yields at 30° and 40° in addition to those at 35°. The effect was studied only in blue light. The results obtained are given in the following table:

TABLE XV

Organic compound	*a*	Quantum efficiency for $\lambda = 4725$ A.U. at		
		30°	35°	40°
Acetone	0·50	0·22	0·24	0·29
	0·10	0·34	0·38	0·44
	0·05	0·37	0·41	0·48
Ether	0·48	0·47	0·52	0·64
	0·12	0·69	0·76	0·95
	0·06	0·74	0·82	1·02

It will be seen that the temperature has quite a marked effect on the quantum yield of the reaction. Also it can be seen that it is more marked for the same rise of temperature at a higher temperature. These results are analogous to those obtained in the study of the effect of temperature on

the velocity constant in case of ethereal solutions of ferric chloride. Such results have been obtained in many cases studied in this laboratory, but the only other case reported in the literature is the work of Kuhn (8). While studying the photo-decomposition of ammonia he obtained a 50 per cent. increase in the quantum yield for every 100 degree rise in temperature. He attributed this to the change in the kinetics of the reaction at higher temperatures.

Summary

1. The photo-reduction of ferric chloride in presence of aqueous acetone and anhydrous ether is a unimolecular reaction.

2. The temperature and the frequency of the exciting radiations have a marked effect on the velocity constant of the reaction.

3. The rate of reaction is directly proportional to the intensity of the incident light.

4. The quantum yield of the reaction increases with dilution of ferric chloride, the temperature and the frequency of the exciting radiations and is of the order of 0·5 for acetone and 1·0 for ether.

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Vol. XVIII, No. 4, Page 190, 2nd para,

6th line *for* Fig. 3 (*a*) *read* Fig. 3 (*b*)

9th line *for* Fig. 3 (*b*) *read* Fig. 3 (*a*)

INDEX TO VOL. XVIII (A)

AUTHORS' INDEX

Asundi, R. K. .. Spectral and collision data of CO^+ and the dissociation energy of carbon monoxide, 8.

Bavdekar, P. R. .. *See* Prasad and Bavdekar.

Bhagavantam, S. .. Normal oscillations of the diamond structure, 251.

Chelam, E. V. .. The normal vibrations in some typical cubic crystals, 257.

.. Normal vibrations of crystal lattices : application of group theory, 283.

.. Character tables for the atomic vibrations in some cubic crystals, 327.

.. The frequency spectrum of the diamond lattice, 334.

Chiplonkar, M. W., and Ranade, J. D. The brightness of the zenith sky during twilight, II, 121.

Deliwala, C. V., Ganapathi, K., and Shirsat, M. V. Chemotherapy of bacterial infections, X, 360.

Desai, T. V., and Guruswamy, S. Opacity changes in gel-forming mixtures during setting, II, 31.

Ganapathi, K. .. Chemotherapy of bacterial infections, IX, 355.

.. *See* Deliwala and others.

Gautam, Lajja Ram, and Jha, J. B. Electrolytic solution pressure of copper wires under strain, 350.

Guruswamy, S. .. *See* Desai and Guruswamy.

Iyengar, K. S. K. .. A tauberian theorem and its application to convergence of Fourier series, 81.

.. New convergence and summability tests for Fourier series, 113.

Jha, J. B. .. *See* Gautam and Jha.

Joshi, S. S., and Purushotham, A. Activation of nitrogen in the presence of mercury, 218.

Kartha, A. R. Sukumaran, and Menon, K. N. The action of grignard reagents on benzopyrones, I, 28.

.. Fixed oil from *Jatropha curcas* (Linn.), 160.

Krishnan, R. S. .. Raman spectra of crystals and their interpretation, 298.

Malurkar, S. L. .. Dynamics of thunderstorms, 20.

Menon, K. N. .. *See* Kartha and Menon.

Menon, P. Kesava .. On arithmetic functions, 88.

Murti, P. Bhaskara Rama, and Seshadri, T. R. Chemical composition of *Calotropis gigantea*, I, 145.

Neelakantam, K., and Rangaswami, S. Colorimetric estimation of boric acid with pentamethylquercetin, 171.

Neelakantam, K., Row, L. Ramachandra, and Venkateswarlu, V. Fluorescence reactions with boric acid and *o*-hydroxycarbonyl compounds, and their application in analytical chemistry, II, 364.

Pandya, Kantilal C., and Pandya, (Miss) Rashmi Bala K. The condensation of aldehydes with malonic acid, XV, 164.

Pandya, (Miss) Rashmi Bala K. *See* Pandya and Pandya.

Panse, T. B., and Paranjpe, A. S. A study of '*Carpasemine*' isolated from *Carica papaya* seeds, 140.

Pant, D. D. .. Luminescence spectra and vibrations in crystal lattices, 309.

Paranjpe, A. S. .. *See* Panse and Paranjpe.

Pasricha, B. R. .. Some integrals involving Humbert function, 11.

Pillai, K. Sankara .. A note on Poisson distribution, 179.

Prakash, Satya, and Rai, Ram Chandra Studies in blue perchromic acid, I, 1.

Prasad, Mata, and Bavdekar, P. R. The photo-reduction of ferric chloride in presence of aqueous acetone and anhydrous ether, 373.

Purushotham, A. .. *See* Joshi and Purushotham.

Rai, Ram Chandra .. *See* Prakash and Rai.

Rajagopalan, S. .. Bacterial chemotherapy, I, II, III, 100, 104, 108.

Ramachandran, G. N. .. Optical theory of chromatic emulsions and of the Christiansen experiment, 67.

.. Fluctuations of light intensity in coronæ formed by diffraction, 190.

.. Modes of atomic vibration in the fourteen Bravais lattices, 266.

.. Modes of vibration of the hexagonal close-packed lattice, 341.

Raman, C. V. .. The vibration spectrum of a crystal lattice, 237.
Ranade, J. D. .. *See* Chiplonkar and Ranade.
Rangaswami, S. .. *See* Neelakantam and Rangaswami.
Rangaswami, S., and Seshadri, T. R. Chemical examination of Indian ergot of the Nilgiris, 206.
Rao, N. S. Subba .. A further study of atmospherics during the monsoon period, 127.
Rao, P. Suryaprakasa, and Seshadri, T. R. Pigments of cotton flowers, IX, 204.
.. Some aspects of the biogenesis of anthoxanthins, 222.
Row, L. Ramachandra .. *See* Neelakantam and others.
Seshadri, T. R. .. *See* Murti and Seshadri.
.. Chemical investigation of Indian fruits, IV, 201.
.. *See* Rao and Seshadri.
.. *See* Rangaswami and Seshadri.
Shirsat, M. V. .. *See* Deliwala and others.
Sunanda Bai, K. .. Interferometric studies of light scattering in binary liquid mixtures, I, 210.
Ta-You Wu .. Excitation processes in the night sky and the aurora, 40.
.. On Maris and Hulburt's ultraviolet light theory of auroræ and magnetic storms, 345.
Venkateswarlu, V. .. *See* Neelakantam and others.

TITLE INDEX

Aldehydes, condensation, with malonic acid, XV (Pandya and Miss Pandya), 164.
Anthoxanthins, some aspects of the biogenesis (Rao and Seshadri), 222.
Atmospherics during the monsoon period, a further study (Rao), 127.
Auroræ and magnetic storms, on Maris and Hulburt's ultraviolet light theory (Ta-You Wu), 345.

Benzopyrones, the action of grignard reagents, I (Kartha and Menon), 28.
Boric acid and *o*-hydroxy-carbonyl compounds, fluorescence reactions, and their application in analytical chemistry, II (Neelakantam and others), 364.
Boric acid, colorimetric estimation, with pentamethylquercetin (Neelakantam and Rangaswami), 171.
Bravais lattices, fourteen, modes of atomic vibration (Ramachandran), 266.

Calotropis gigantea, chemical composition, I (Murti and Seshadri), 145.
Carica papaya seeds, '*Carpasemine*' isolated from, a study (Panse and Paranjpe), 140.
Chemotherapy, bacterial, I, II, III (Rajagopalan), 100, 104, 108.
Chemotherapy of bacterial infections, IX (Ganapathi), 355 ; X (Deliwala and others), 360.
Chromatic emulsions and the Christiansen experiment, optical theory (Ramachandran), 67.
CO^{+}, spectral and collision data, and the dissociation energy of carbon monoxide (Asundi), 8.
Copper wires under strain, electrolytic solution pressure (Gautam and Jha), 350.
Coronæ formed by diffraction, fluctuations in light intensity (Ramachandran), 190.
Cotton flowers, pigments, IX (Rao and Seshadri), 204.
Crystal lattices, luminescence spectra and vibrations (Pant), 309.
Crystal lattices, normal vibrations : application of group theory (Chelam), 283.
Crystal lattice, the vibration spectrum (Raman), 237.
Crystals, Raman spectra, and their interpretation (Krishnan), 298.
Crystals, some cubic, character tables for the atomic vibrations (Chelam), 327.
Crystals, some typical cubic, the normal vibrations (Chelam), 257.

Diamond lattice, the frequency spectrum (Chelam), 334.
Diamond structure, normal oscillations (Bhagavantam), 251.

Ergot, Indian, of the Nilgiris, chemical examination (Rangaswami and Seshadri), 206.

Ferric chloride, the photo-reduction, in presence of aqueous acetone and anhydrous ether (Prasad and Bavdekar), 373.

Fourier series, a tauberian theorem and its application to convergence of (Iyengar), 81.

Fourier series, new convergence and summability tests for (Iyengar), 113.

Fruits, Indian, chemical investigation, IV (Seshadri), 201.

Functions, arithmetic (Menon), 88.

Gel-forming mixtures, opacity changes, during setting, II (Desai and Guruswamy), 31.

Humbert function, some integrals involving (Pasricha), 11.

Jatropha curcas (Linn.), fixed oil from (Kartha and Menon), 160.

Lattice, hexagonal close-packed, modes of vibration (Ramachandran), 341.

Light scattering in binary liquid mixtures, interferometric studies, I (Sunanda Bai), 210.

Night sky and the aurora, excitation processes (Ta-You Wu), 40.

Nitrogen, activation, in the presence of mercury (Joshi and Purushotham), 218.

Perchromic acid, blue, studies (Prakash and Rai), 1.

Poisson distribution, a note (Pillai), 179.

Thunderstorms, dynamics (Malurkar), 20.

Zenith sky, the brightness, during twilight, II (Chiplonkar and Ranade), 121.

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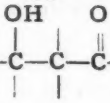
CONTENTS

On Maris and Hulburt's Ultraviolet Light Theory of Auroræ and Magnetic Storms . . . . . TA-YOU WU 345

Electrolytic Solution Pressure of Copper Wires under Strain . . . . . LAJJA RAM GAUTAM AND J. B. JHA 350

Chemotherapy of Bacterial Infections. IX. Synthesis of Some Sulphathiazole Derivatives . . . . . K. GANAPATHI 355

Chemotherapy of Bacterial Infections. X. 2-Acetsulphanilimido-3-acetsulphanilylthiazolone and 2-Diacetsulphanilylamidothiazole. A New Route to Sulphathiazole . . . . . C. V. DELIWALA, K. GANAPATHI AND M. V. SHIRSAT 360

Fluorescence Reactions with Boric Acid and *o*-Hydroxy-Carbonyl Compounds, and Their Application in Analytical Chemistry. Part II. Detection of  in Aromatic Compounds containing C, H and O only . . . . . K. NEELAKANTAM, L. RAMACHANDRA ROW AND V. VENKATESWARLU 364

The Photo-Reduction of Ferric Chloride in Presence of Aqueous Acetone and Anhydrous Ether . . . . . MATA PRASAD AND P. R. BAVDEKAR 373